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Research Proposal for the use of Neutron Science Facilities

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Program Advisory Subcommittee: Nuclear Technology
Focus Area:

Flight Path/Instrument: Target 2 / Blue Room
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Days Recommended: 0
Dates Desired:
Impossible Dates:

TITLE
Production and Recovery of Mo-99 From Low Enriched Uranyl Nitrate Solutions

☐ Continuation of Proposal #:

☐ Ph.D Thesis for:

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RESEARCH AREA

- ☐ Biological and Life Science
- ☐ Chemistry
- ☐ National Security
- ☐ Earth Sciences
- ☐ Engineering
- ☐ Environmental Sciences
- ☒ Nuc. Physics/chemistry
- ☐ Astrophysics
- ☐ Few Body Physics
- ☐ Fund. Physics
- ☐ Elec. Device Testing
- ☒ Dosimetry/Med/Bio
- ☐ Earth/Space Sciences
- ☐ Materials Properties/Test
- ☐ Other:
- ☐ Mat'l Science (incl Cond Matter)
- ☐ Medical Applications
- ☐ Nuclear Physics
- ☐ Polymers
- ☐ Physics (Excl Condensed Matter)
- ☐ Instrument Development
- ☐ Neutron Physics
- ☒ Fission
- ☒ Reactions
- ☐ Spectroscopy
- ☒ Nuc. Accel. Reactor Eng.
- ☐ Def. Science/Weapons Physics
- ☐ Radiography
- ☒ Threat Reduction/Homeland Sec.
- ☐ Other:

FUNDING AGENCY

- ☐ DOE/BES
- ☐ DOE/OBER
- ☒ DOE/NNSA
- ☐ DOE/NE
- ☐ DOE/SC
- ☐ DOE/Other
- ☐ DOD
- ☐ NSF
- ☒ Industry
- ☐ NASA
- ☐ NIH
- ☐ Foreign:
- ☐ Other US Gov't:
- ☐ Other:

PUBLICATIONS

Publications:

M. Mocko, G. Muhrer, Ch.T. Kelsey, M.A. Duran, F. Tovesson, "Experimental measurement of the neutron time-emission spectra at the Manuel Lujan Jr. Neutron Scattering Center," Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Volume 632, Issue 1, 11 March 2011, Pages 101-108.

Abstract: S1555_blue_room_pr.pdf

By electronic submission, the Principal Investigator certifies that this information is correct to the best of their knowledge.

Safety and Feasibility Review *(to be completed by LANSCE Instrument Scientist/Responsible)*

☐ **No further safety review required** ☐ **To be reviewed by Experiment Safety Committee**

☐ **Approved by Experiment Safety Committee, Date:**

Recommended # of days:	**Change PAC Subcommittee and/or Focus Area to:**	**Change Instrument to:**

Comments for PAC to consider:

Instrument scientist signature: **Date:**

Production and Recovery of Mo-99
From Low Enriched Uranyl Nitrate Solutions

Introduction

The daughter product of Mo-99, Tc-99m, is the most commonly used radioisotope for nuclear medicine. This radioisotope is used in approximately two-thirds of all nuclear medicine imaging procedures, amounting to approximately 50,000 diagnostic nuclear medicine procedures performed every day in the United States (US). Until recently, the entire US supply of Mo-99 for nuclear medicine has been produced in two aging foreign reactors using highly enriched uranium (HEU) targets. Recent maintenance and repair shutdowns of these reactors have significantly disrupted the supply of Mo-99 in the US and much of the rest of the world. Additionally, a forecasted supply shortage of HEU for targets in the European production reactors is anticipated to cause significant future supply disruptions as well.

The National Nuclear Security Administration's (NNSA's) Global Threat Reduction Initiative (GTRI, NA-21), in partnership with commercial entities and the US national laboratories, is working to address the need for a reliable domestic supply of Mo-99 for nuclear medicine while also minimizing the civilian use of HEU. The objective of the effort is to aid the development of a reliable, domestic, commercial supply of Mo-99 that avoids a single point of failure and does not require the use of HEU. Towards this effort the GTRI is currently funding exploration into 5 technology pathways for stable production of Mo-99, which are:

- Low enriched uranium (LEU) targets in fission reactors
- LEU solution reactors
- Neutron capture in Mo-98 targets in a nuclear reactor
- Photon capture in Mo-100 using an electron accelerator and a bremsstrahlung target
- Subcritical LEU solution target driven with a DT neutron generator.

LEU targets will have at least a 5 times higher uranium concentration compared to HEU targets for a given amount of Mo-99 production, and significant production and separation uncertainties remain in the LEU separations chemistry, which constitute 3 of the 5 approaches that the GTRI is currently investigating. To address these uncertainties and support the GTRI mission for stable domestic supply of Mo-99, we propose a set of experiments utilizing WNR Target 2 (blue room) equipped with a spallation target to irradiate LEU samples for experiments on Mo-99 separation chemistry. This will be a modified version of an experiment we will conduct shortly with a 9 MeV electron accelerator as part of our NA-21 funded work, however, indications are that a 50 times higher Mo-99 yield can be achieved in the blue room, significantly improving the quality of the results produced from subsequent separations chemistry experiments.

The primary objective of this experiment is to produce samples and use them for Mo-99 recovery tests relevant to GTRI (NA-21) sponsored research and development into LEU production of Mo-99. A secondary objective of this experiment is to provide a relevant benchmark for radiation transport and transmutation calculations supporting the design of such facilities.

Background

We have designed an experimental target-moderator-reflector-shielding (TMRS) assembly for the production of Mo-99 in uranyl nitrate solutions using photons from a 15 μA, 9 MeV Varian Linatron that we plan to operate in March 2011. Photoneutrons produced in beryllium and heavy water provide an internal neutron source for fission production of Mo-99 in uranyl nitrate solution samples. Both light water (LWTR) and heavy water (HWTR) based uranyl nitrate solutions are being investigated as part of our NA-21 funded research into the subcritical LEU solution target approach. We have calculated that an external spallation neutron source generated by 800 MeV protons on tungsten can result in 50 times the Mo-99 yield at only 50% of the Linatron beam power using the same assembly.

A photograph of the experimental setup using the Varian Linatron is shown in Figure 1. The basic assembly design consists of stacked 5L jerrycans holding HWTR, as shown in the figure. This HWTR will be surrounded by a beryllium and polyethylene (PE) reflector. This reflector will be surrounded by 5% borated polyethylene (BPE) neutron shielding. The total mass of the assembly will be about 1000 Kg. The external dimensions will be approximately 1 m x 1 m x 1 m.

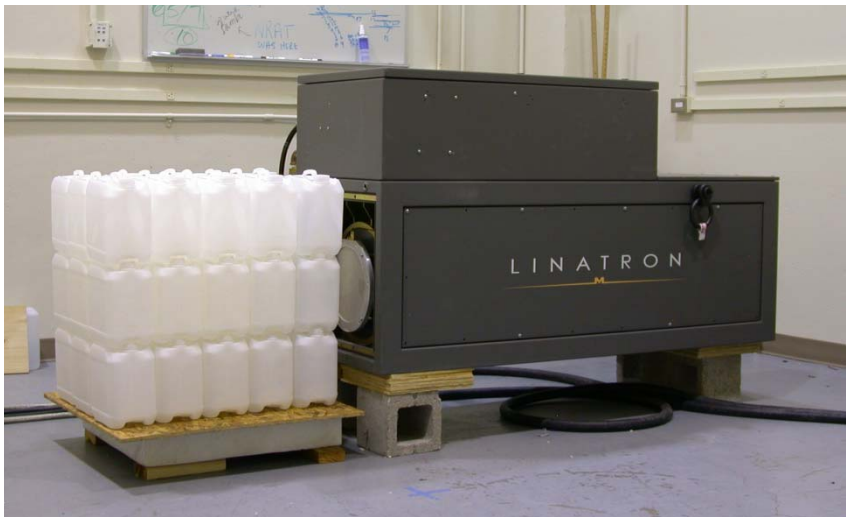
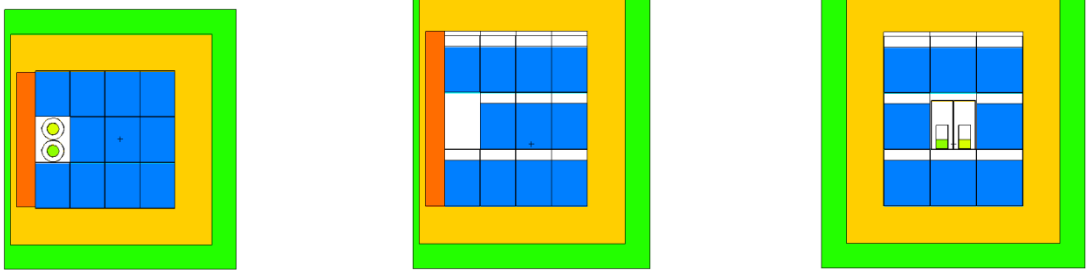


Figure 1: Photograph of the Linatron irradiation experiment showing the 5L jerrycans stacked in front of the 9 MeV x-ray producing electron accelerator.

Figure 2 presents MCNPX model plots. The HWTR moderator material is contained in 35, 5-liter stackable polyethylene jerrycans, one of which is shown in Figure 3. The can stack is 3 cans wide, 3 cans high and 4 cans deep (a slightly deeper stack is shown in Figure 1). One can is omitted from the stack to accommodate two uranyl nitrate solution samples. Similar to our experiments using the Linatron, it is proposed that one sample will be a HWTR solution and the other a light water (LWTR) solution. Each sample will be 70 ml in volume with a uranium concentration of 35 g/l (2.45 g U per sample) and U-235 enrichment of 19%. Uranium will be present as uranyl nitrate with a solution acidity of 0.1 mol/L. Sample containers will be 125 ml high density polyethylene (HDPE) bottles, placed in 1000 mL HDPE bottle secondary containment. Options for reduction of the secondary containment volume to 500 mL are currently being evaluated, as is secondary containment for the HWTR moderator in the jerry cans if necessary.



Horizontal section. Front to back vertical section. Right to left vertical section.

Figure 2: MCNPX model of experimental target-moderator-reflector-shielding assembly (green = BPE, orange = Be, yellow = PE, blue = HWTR, light green = HWTR sample, light yellow = LWTR sample).

Figure 3: 5-liter jerry can.

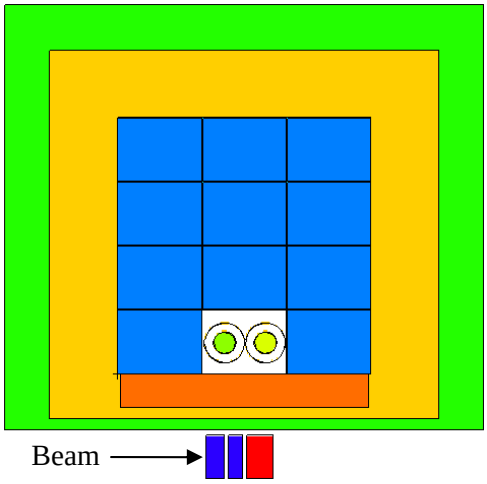


Figure 4: Model plot with proton beam and targets (dark blue = tungsten, red = steel).

The proton beam target will consist of two tungsten cylinders and one steel cylinder, all 10 cm in diameter, as illustrated in Figure 4. The tungsten targets are disks stacked in aluminum cans. One is 4 cm thick tungsten and the other 3.1 cm. The steel target is 6 cm thick. These are the same targets that the LANSCE-LC spallation physics team has been using for Target 2 moderator development experiments.

The MCNPX and CINDER codes were used to calculate radionuclide inventories for the assembly components and targets assuming 80 nA beam delivery for irradiation times of 1 to 5 days. Calculated Mo-99 activities in the samples are listed in Table 1. We would like to produce as much Mo-99 as practical for test recovery tests. However, because of its 2.75-day half-life irradiation beyond about 5 days adds relatively little to the activity as equilibrium is approached. For comparison to LANSCE experimental area radioactive material-at-risk (MAR) limits the total mass in plutonium equivalent grams (PEGs) in the experimental assembly and targets at the end of each of the assumed irradiation periods was also calculated. The MAR values are all substantially below 0.1 PEGs and should not require tracking at WNR. The heavy water moderator material that will be used has tritium in it. The tritium activity concentration in the heavy water is 103 μCi/l, which is negligible with respect to MAR limits and the experiment will not significantly add to the tritium content.

Post irradiation 30 cm exposure rates were conservatively estimated based on CINDER produced decay radiation spectra. These values are listed in Table 2. The only components expected to have exposure rates greater than 1 mR/h after 3 hours of decay time are the samples and the targets. The exposure rate estimates are listed in Table 3 for samples and Table 4 for targets. After 3 hours sample exposure rates are expected to be less than 100 mR/h. Target exposure rates are substantially higher. Typically when these targets are used in the blue room 24 hours is allowed to pass before entry and then the targets are immediately transferred to a shielded cask for storage. The target inventory and exposure rate calculations ignore previous irradiations. The last was during the 2010 run cycle. Long lived activity still present will not contribute significantly to future post irradiation dose rates. After irradiation we plan to transfer the samples to TA-48 for measurements and Mo-99 recovery experimentation. The details of the Mo-99 recovery experiments are discussed in detail in the next section.

days on at 80 nA	Mo-99 activity after decay time (mCi)					
	0.00 h	1.00 h	3.29 h	8.53 h	20.53 h	48.00 h
HWTR sample						
1	0.27	0.26	0.26	0.24	0.21	0.16
2	0.47	0.47	0.46	0.43	0.38	0.29
3	0.63	0.63	0.61	0.58	0.51	0.38
4	0.76	0.75	0.73	0.69	0.61	0.46
5	0.86	0.85	0.83	0.78	0.69	0.52
LWTR sample						
1	0.26	0.26	0.25	0.24	0.21	0.16
2	0.46	0.46	0.45	0.42	0.37	0.28
3	0.62	0.61	0.60	0.57	0.50	0.37
4	0.74	0.73	0.72	0.68	0.60	0.45
5	0.84	0.83	0.81	0.76	0.67	0.51

Table 1: Calculated post irradiation Mo-99 activities in samples.

Days on at 80 nA	PEG at end of irradiation
1	7.59E-04
2	8.81E-04
3	9.69E-04
4	1.04E-03
5	1.10E-03

Table 2: Calculated MAR at end of irradiation.

days on at 80 nA	30 cm sample exposure rates after decay time (mR/h)				
	1.00 h	3.29 h	8.53 h	20.53 h	48.00 h
HWTR sample					
1	108	52	26	13	5.4
2	118	61	34	18	8.9
3	123	66	38	22	12
4	127	70	42	25	14
5	130	72	44	27	16
LWTR sample					
1	105	51	25	12	5.2
2	115	60	33	18	8.7
3	120	65	37	22	11
4	124	68	41	24	13
5	126	71	43	27	15

Table 3: Estimated post irradiation sample exposure rates.

Experiment

At TA48 we have access to 19% enriched U_3O_8 of an acceptably chemical purity. This can be dissolved in nitric acid and standard chemical manipulations can then be employed to generate the target solutions for irradiation. Solution pH(D) will be measured for both solutions, noting that the accuracy of the pH (HNO_3) measurement will be greater than that of the pD (DNO_3) measurement. Uranium speciation will be confirmed by absorption spectroscopy (Ultra Violet/visible – UV/vis) and uranium concentration will be determined both spectroscopically and by ICP-AES (Inductively Couple Plasma-Atomic Emission Spectroscopy). The multiply contained samples will then be shipped for irradiation at TA-53.

We will transfer the TMRS assembly from the Linatron experiment's location at TA3 to the blue room. We will also provide a stand that will raise the assembly to beam line elevation and hold the targets. The samples with be placed inside with bare and cadmium covered gold foils from LANSCE-LC for thermal flux measurement. We require no particular beam pulse structure or profile. We only request the maximum average current with an arbitrarily small spot size delivered centrally on the target face.

days on at 80 nA	30 cm target exposure rates after decay time (R/h)				
	1.00 h	3.29 h	8.53 h	20.53 h	48.00 h
first tungsten target					
1	15	9.2	6.2	3.7	1.8
2	18	12	8.8	5.7	3.0
3	20	14	10	6.9	3.9
4	21	15	11	7.8	4.5
5	22	16	12	8.5	4.9
second tungsten target					
1	10	6.2	4.2	2.5	1.2
2	12	8.1	5.9	3.8	2.0
3	13	9.3	6.9	4.6	2.5
4	14	10	7.6	5.2	2.9
5	14	11	8.1	5.6	3.2
steel target					
1	2.2	1.3	0.6	0.3	0.2
2	2.5	1.5	0.8	0.5	0.4
3	2.7	1.7	1.0	0.6	0.5
4	2.9	1.9	1.2	0.8	0.6
5	3.0	2.0	1.3	0.9	0.8

Table 4: Estimated post irradiation target exposure rates.

We plan to wait 24 hours for dose rates to drop after irradiation prior to entering the blue room to retrieve the samples, activation foils and the TMRS assembly. The TMRS assembly will be returned to TA-3. We will have RP-1 at TA-53 measure sample dose rates and perform gamma spectroscopy for the activation foils.

48 hours post irradiation the samples will be returned from TA-53 to TA-48. The change in pH(D) will be measured and 20 mL of each sample set aside for analysis, both UV/vis to confirm uranium speciation and gamma spectroscopy. 50 mL of sample will then be passed through a column containing 10 cm^3 alumina, pre- conditioned with 0.1 M HNO_3 for the LWTR sample or 0.1 M DNO_3 for the HWTR sample. The LWTR column will then be washed with 5 column volumes of 0,1 M HNO_3, then H_2O and finally 1 M NH_3OH. The HWTR column will then be washed with 1 column volume of 0.1 M DNO_3, 4 column volumes of 0.1 M HNO_3, and 5 column volumes of both H_2O and 1 M NH_3OH. 10 mL fractions will be collected and each fraction will be analyzed for uranium (a combination of UV/vis spec, ICP-AES and gamma spectroscopy) and fission products (gamma spectroscopy). For selected samples gamma spectra will be rerecorded over several days, and perhaps even weeks, to allow time for the decay of 'masking' short lived isotopes from longer lived radionuclides of interest.

From the TA-48 side of the experiment we aim to provide the following information:

1. An experimental measurement of the total amount of Mo-99 present in each sample.
2. The effect of irradiation on pH(D).

3. A profile of Mo-99 and uranium concentration within the separated fractions and hence both % Mo-99 recovery in the product fraction(s) and the ratio of U/Mo-99 in this product.
4. Analysis of other important radioisotopes (e.g. I-131) that could potentially contaminate the Mo-99 product.
5. Preliminary evaluation of an alumina column as the separation method for Mo-99 recovery from a homogenous solution reactor and a recommendation of additional separations steps that may be required.

On the TA-53 side we plan to provide:

1. An experimental measurement of the thermal flux at sample location.
2. Measurement of the sample dose rates.
3. Using actual beam history obtained from DSRP, MCNPX-CINDER calculations of sample location thermal flux, sample radionuclide inventories, and sample dose rates.
4. Comparisons of measurements and calculations in a benchmark report.

Justification

Following irradiation, Mo-99 produced from the fissioning of U-235 (a.k.a. fission product moly), must be separated from the excess uranium and other fission/neutron capture products in the target (Mo-99 has a 6% fission yield). Ideally, one would like to separate the Mo-99 produced from LEU targets through the most common method currently used to process HEU targets, running the dissolved target solution through a simple alumina column. There is experimental evidence in the literature that this approach may not be viable, and it should also be noted that additional purification steps are required for target purification. Nevertheless, an alumina based separation is the logical starting point as there is very limited data related to processing of irradiated LEU solutions, and no known data on processing irradiated heavy water LEU solutions. To gauge the effectiveness of the separation, and the extent/nature of the chemistry challenges that need to be overcome, we need more accurate and process realistic experimental data. Irradiating solutions with the Linatron will be our first step in this investigation. Subsequently, Mo-99 concentrations at least 20 times higher than those produced with the Linatron will be possible in the blue room. A Mo-99 activity of greater than 0.1 mCi per sample will enable us to more accurately account for losses of material in non-product fractions after separation, and lower gamma spectroscopy count times for selected analyses. Also, this activity level will allow us to monitor the distribution of additional isotopes that could contaminate the Mo-99 product stream. Irradition times using the Linatron are limited due to the nature of the device (designed for radiography) and availability of operating personnel. Several day irradiations are possible in the blue room, which will be much closer to conditions expected in a production facility.

We request 5 days of 800 MeV linac beam at 80 nA for optimal Mo-99 yield. We plan 1 day of post irradiation cool down time and expect a half day each for setup and take down of the assembly. We therefore request 7 days in the blue room.

Safety

The following are hazards we have identified and controls we are anticipating:

1. External radiation exposure – the targets are the greatest exposure hazard. We plan a post irradiation cool down period to minimize doses and the first take down step will be to return targets to shielding for storage.
2. Radioactive contamination – we are planning primary and secondary containment for all liquids in the experiment.
3. Sample pressurization – we expect that the 125 ml sample containers for 70 ml sample volumes will accommodate gaseous fission product buildup. We are additionally providing secondary containment.
4. Be oxide contamination – the Be metal in the assembly will be wrapped in plastic for containment.
5. Polyethylene fire hazard – we do not plan to clad the polyethylene materials but expect the transient combustible load will be acceptable.
6. Transportation between TA-53 and TA-48 – transports will be undertaken in full accordance with DOT regulations and LANL requirements. As both samples are solutions they will be packaged in certified Viking containers. Greater than 50 g heavy water in one sample is an accountable quantity of material and thus we will coordinate shipment with Nuclear Materials Custodians at both ends. Shipments will be undertaken by OS-PT (Packaging and Transportation).

Lessons learned from our March Linatron experiment will be applied to the blue room experiment.

Security

Heavy water in > 50g quantities is accountable at LANL. For this experiment the heavy water will be located in sealed 5-liter jerrycans which will be individually weighed before and after the experiment for material accountability. Similarly, the heavy water based uranyl nitrate sample will be in a sealed container and weighed before and after the experiment for material accountability. Accountable shipping methods will also be used for transporting the accountable heavy water containing items between TAs at the lab. Alternatively, for the heavy water based uranyl nitrate sample, it may be possible to create a sample using < 50 g of heavy water. This sample volume would be about 45 mL, which is only half of what we are using currently.

U-235 in quantities > 0.5 g is accountable at LANL. Each sample will contain < 0.5 g of U-235 and will therefore not be accountable.